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Determination of Hydrocyanic Acid and Free Cyanide in Aqueous Solution

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Microgram-per-liter concentrations of HCN in aqueous solutions were determined directly by two methods: bubbling compressed air through a solution to displace a small quantity of HCN, which was collected in a glass bead concentration column, or allowing some HCN to diffuse from an enclosed solution into dilute NaOH in a dish suspended above the solution. The separated and concentrated cyanide was determined colorimetrically. The HCN concentration was calculated from linear calibration curves that related the determined HCN displacement rate or quantity of HCN collected to the known concentration of HCN for standard cyanide solutions. The linear relationship between pK for HCN (aq) and 1/temperature in degrees Kelvin was defined. Thus the fraction of free cyanide (i.e., $HCN + CN^-$) as HCN for specific conditions of temperature and pH could be determined. These procedures for determining HCN in various waters and wastewaters were accurate, precise, and not susceptible to common interfering substances.

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Determination of Hydrocyanic Acid and Free Cyanide in Aqueous Solution

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Microgram-per-liter concentrations of HCN in aqueous solutions were determined directly by two methods: bubbling compressed air through a solution to displace a small quantity of HCN, which was collected in a glass bead concentration column, or allowing some HCN to diffuse from an enclosed solution into dilute NaOH in a dish suspended above the solution. The separated and concentrated cyanide was determined colorimetrically. The HCN concentration was calculated from linear calibration curves that related the determined HCN displacement rate or quantity of HCN collected to the known concentration of HCN for standard cyanide solutions. The linear relationship between pK for HCN (aq) and 1/temperature in degrees Kelvin was defined. Thus the fraction of free cyanide (i.e., HCN + CN^-) as HCN for specific conditions of temperature and pH could be determined. These procedures for determining HCN in various waters and wastewaters were accurate, precise, and not susceptible to common interfering substances.

Cyanides are formed and extensively used in industrial processes and occur in effluents from various sources. Simple cyanides (e.g., NaCN) readily react with certain heavy-metal salts, forming complex cyanides. Hydrocyanic acid (HCN) is formed in solutions of these salts through dissociation or decomposition of the complex metallocyanide anions and hydrolytic reaction with water by the liberated cyanide ions. The acute toxicity to aquatic organisms of dilute solutions of various simple cyanides and metal–cyanide complexes is usually attributed almost entirely to the concentration of HCN (*1*, *2*), with minimal contribution from the cyanide ion (CN^-) and most metallocyanide anions.

The concentration of free cyanide (i.e., HCN + CN^-) in less stable metal cyanide complex solutions and that of HCN alone cannot be accurately determined by conventional analytical methods for cyanide. Blaha's (*3*) mathematical approach of computing the concentration of HCN in natural water is of questionable accuracy because the accepted equilibrium constants of the metallocyanide ions may be inaccurate. Also, the kinds and concentrations of metallic compounds and complex ions present, and the degree of their equilibration, are uncertain. Since a determination of total cyanide may not be a reliable index of cyanide toxicity, a need exists to measure directly the concentration of HCN in the microgram-per-liter range in evaluating the adverse effects on aquatic biota of cyanide wastes discharged to natural waters.

Methods have been proposed to estimate free cyanide in an aqueous sample by using the Roberts and Jackson distillation procedure (*4*), a microdiffusion cell (*5*, *6*), or a gas-permeable membrane (*7*) to isolate and concentrate HCN in dilute alkali. These methods, however, require acidification of the sample with the conversion to HCN of simple cyanides and most likely some portion of certain metallocyanides.

Several methods have been described for the direct determination of HCN in aqueous solution. Methods based on establishing a distribution equilibrium between the concentration of HCN in water and in air or nitrogen bubbled through the water were described by Worley and Browne (*8*), Schneider and Freund (*9*), Claeys and Freund (*10*), and Nelson and Lysyj (*11*). The methods differ in the ways in which the displaced HCN is trapped and then measured. Montgomery et al. (*12*) developed a procedure for determining HCN whereby a small proportion of HCN is extracted with 1,1,1-trichloroethane, transferred into sodium pyrophosphate, and determined colorimetrically. In a relatively untested method (*13*, *14*) molecular HCN is allowed to diffuse for a fixed time period from a sample in an airtight container into weak alkali contained in an open, shallow dish exposed to the atmosphere above the sample. The cyanide content in the alkali solution is then determined colorimetrically.

The methods in which vapor-phase equilibration is used require costly and special analytical apparatus and a fairly large sample size. The extraction method uses a hazardous organic solvent, and its applicability for determining HCN in certain metal cyanide complex solutions is questionable. Therefore, the main objective of this study was to develop a convenient and generally interference free analytical procedure for the direct determination of microgram-per-liter concentrations of HCN in water and wastewater.

EXPERIMENTAL SECTION

Determination of Cyanide. Cyanide was determined by titration with silver nitrate and by a slightly modified colorimetric method which uses chloramine-T and pyridine–barbituric acid reagents (*15*). The titrimetric procedure was used to standardize stock cyanide solutions prepared from sodium cyanide (NaCN). Dilute cyanide solutions were prepared by quantitative dilution of a standardized stock. The reagents used in the colorimetric method were prepared as directed (*15*) except that the pH of the NaOH absorbent solution was reduced to about 5.6 with acetic acid just before addition of the chlormine-T reagent. Standard cyanide solutions were prepared and analyzed spectrophotometrically to establish a calibration curve for each set of test conditions. Since varying the NaOH concentration, reagent volumes, etc. may affect color development, an effort was made to maximize the sensitivity of the method by adjusting test conditions. A Beckman DB-G spectrophotometer equipped with digital display and 1-cm cell-path length was used to measure color intensity.

Direct Determination of HCN. Methods based upon solution–air distribution of HCN and analysis of the displaced and concentrated HCN were used to eliminate interference from most components in solution and interaction between the color-development reagents and complex cyanides. With both procedures the proportion of HCN extracted from a test solution was so small (less than 4%) that the complex equilibria involving other cyanide forms was not appreciably altered.

The apparatus used to determine HCN by the vapor-phase-equilibration method was previously described by Broderius and Smith (*2*), where they used a similar procedure for the direct determination of H_2S. The method for determining HCN uses a gas regulator and flow meter, a temperature regulated sparging chamber, and a glass bubbler through which finely dispersed air is bubbled at 25–300 mL/min in 20 L of test solution. A glass bead concentration column coated with about 0.4 mL of 1.0 N NaOH is used to collect the displaced HCN, and a water displacement bottle measures the volume of air dispersed in the sample and passed through the column. At the end of the collection period the cyanide absorbed in the concentration column is washed off with three 5-mL washings of deionized water into a 25-mL volumetric flask for colorimetric analysis.

The HCN concentration in a solution is calculated from the quantity of HCN collected in a column and by reference to a calibration curve relating the micrograms of HCN displaced per liter of air dispersed with the known HCN concentration in standard solutions of the same temperature. The standard HCN test solutions were prepared by diluting stock cyanide solutions with deionized water and then lowering the pH with HCl to about 5.5, where essentially all the free cyanide is present as HCN. The actual concentration of free cyanide in these standard solutions was determined by the direct colorimetric procedure during the bubbling period.

The apparatus used to determine HCN by the diffusion method consists of a 2.8-L Fernbach flask (Corning 4420) fitted with an airtight No. 13 neoprene rubber stopper and the bottom section of a petri dish (Corning 3160, 60 × 15 mm) attached by silicone cement to a solid glass support rod (Figure 1). The isolation and concentration of HCN from an aqueous solution is accomplished by adding 1.5 L of sample to the flask and sealing with a stopper. After a short equilibration period either 8.5 or 20.5 mL of 0.02 N NaOH is pipetted through a small hole in the large stopper into the petri dish suspended in the air space above the sample. The system is sealed, and the HCN diffusing from the surface of the test solution is absorbed into the alkali solution. The air space between the sample and alkali serves to separate the

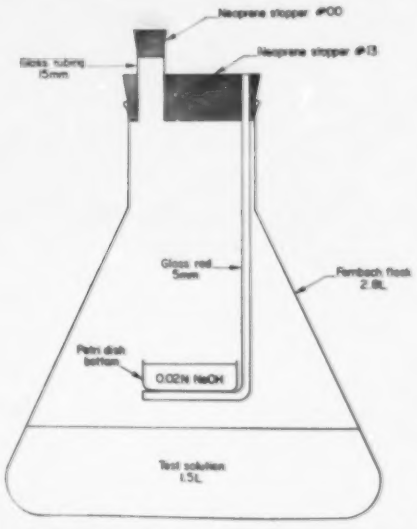

Figure 1. Apparatus used to isolate and concentrate molecular hydrogen cyanide by the diffusion procedure.

nonvolatile and ionic species in solution from the collected HCN. A 2-h collection period is generally sufficient to allow for an analytically measurable amount of HCN to be transferred from the sample to the NaOH. The small stopper in the lid is then removed, and an 8- or 20-mL aliquot of alkali absorbent containing the dissolved HCN is transferred to a 10- or 25-mL volumetric flask, respectively. The solution is acidified to about pH 5.6 with 3 or 6 drops of 2.25 N acetic acid, respectively. Four drops of chloramine-T solution (1.0 g/100 mL) are added, mixed, and allowed to stand for about 2 min. A single solution combining a phosphate buffer and chloramine-T can be used to lower the pH of the 0.02 N NaOH and to halogenate the cyanide (*15*). Then 1.0 or 2.5 mL, respectively, of the pyridine–barbituric acid reagent is added and mixed, and the volume is made to the mark with deionized water. After about 10 min the intensity of color produced is measured at 582 nm against a blank. The cyanide content expressed as HCN is determined from a suitable calibration curve.

The concentration of HCN in a sample is determined from a calibration curve defined from tests performed with standardized NaCN solutions prepared with deionized water and at about pH 6. The tests with the standard solutions are conducted at the same time and under the same conditions as those for the unknown samples. In this way standard solutions are treated as samples, and slight changes in factors that may affect the diffusion of HCN from a test solution would be reflected in the calibration curve. A constant-temperature water bath may be used to ensure temperature control of the test solutions during the collection period.

Nickel and silver cyanide complex stock solutions were prepared by adding Ni(II) or Ag(I) salt solutions to concentrated NaCN solutions until the first definite but persistent turbidity due to precipitated metal cyanide was observed.

RESULTS AND DISCUSSION

Direct Determination of HCN. The concentration of HCN in an aqueous solution was determined by either of two methods of separating a small portion of HCN from a sample and collecting the evolved cyanide in an alkaline solution. Experiments with the vapor-phase-equilibration method demonstrated that with a constant air-flow rate of 50 mL/min there was essentially no effect on HCN displacement rate when the dispersion depth for a glass frit of medium or coarse porosity ranged from 15 to 90 cm. During any determination the column height varied at most only a few centimeters within this range. The efficiency of HCN displacement from a solution by a disperser at a depth of 50 cm was essentially constant when the rate of air flow varied between 25 and 300 mL/min.

Table I. Reproducibility in Amount of HCN Collected by the Diffusion Procedure from Standard Cyanide Solutions

HCN concn, μg/L	HCN collected,[a] μg		
	mean	std dev	RSD
	8.5 mL 0.02 N NaOH		
1.31	0.0809	0.004 55	5.62
2.14	0.118	0.005 76	4.89
4.46	0.218	0.012 3	5.62
7.86	0.416	0.023 3	5.60
27.2	1.08	0.043 7	4.06
38.9	1.35	0.063 6	4.71
	20.5 mL 0.02 N NaOH		
3.46	0.174	0.013 0	7.46
4.80	0.262	0.014 1	5.36
10.1	0.555	0.021 2	3.81
26.9	1.36	0.060 4	4.45
52.4	2.78	0.128	4.58

[a] HCN collected by 8.5 or 20.5 mL of 0.02 N NaOH in 2 h from 1.5-L solutions at 22 °C. Results are for six replicate determinations at each HCN concentration.

The rate at which HCN is displaced by dispersed air was determined at six temperatures for each of six different solutions containing known HCN concentrations ranging from about 0.01 to 0.20 mg/L. The mean distribution coefficients relating the micrograms of HCN displaced per liter of air dispersed through a solution to the known HCN concentration in milligrams-per-liter for mean temperatures of 5.0, 10.1, 15.0, 20.0, 24.9, and 30.0 °C were 1.955, 2.372, 2.897, 3.513, 4.112, and 4.922, respectively. The corresponding standard deviations were 0.0641, 0.0715, 0.0639, 0.0620, 0.131, and 0.0519. These values correspond to a precision estimate expressed as an overall mean relative standard deviation of 2.42 ± 0.90%. The lower limit of detection of this method is governed by the bubbling time and rate. With a 3-h collection period at a dispersion rate of 100 mL/min and selecting 0.020 as an easily measured absorbance change for a 1-cm path length, the detection limit is approximately 1.3 μg HCN/L.

The distribution coefficients (Y) are log linear with temperature in degrees Celsius (X), and a regression equation defining this relationship with $R^2 = 0.994$ is $\log Y = 0.2153 + 0.01608X$. This equation was used to calculate the concentration of HCN in a test solution when temperature and micrograms of HCN displaced per liter of air dispersed through the solution were determined.

The isolation and concentration of cyanide by the diffusion procedure were shown to be particularly suitable as a simple and convenient method for the determination of low concentrations of HCN in aqueous solution. The reproducibility of HCN measurements, as defined by the relative standard deviation in amount of HCN collected, was determined for a 2-h diffusion period from 1.5-L solutions at 22 °C. The results for collection volumes of 8.5 or 20.5 mL of 0.02 N NaOH from six replicate determinations at each of several known HCN concentrations are presented in Table I. In the concentration range of about 1–50 μg HCN/L the precision of this method expressed as an overall mean relative standard deviation is 5.08 ± 0.64% and 5.13 ± 1.41% for 8.5- and 20.5-mL collection volumes, respectively. The linear relationships between the quantities (μg) of HCN collected (Y) by 8.5- and 20.5-mL volumes and the HCN concentration (μg/L) in a test solution (X) at 22 °C can be represented by $Y = 0.0758 + 0.0342X$, $R^2 = 0.989$, and $Y = -0.0035 + 0.0527X$, $R^2 = 0.999$, respectively (Table I). The lower limit of detection is governed by the diffusion time and test temperature. When the collection period is 2 h for solutions at 22 °C, and 0.020 is selected as an easily measured absorption change for a 1-cm path length, the detection limit is approximately 1.0 and 1.6 μg HCN/L for the 8.5- and 20.5-mL collection volumes, respectively.

The amount of HCN collected by the diffusion procedure is temperature dependent. This effect is minimal, however, in the temperature range of 15 °C to about 22 °C. At higher temperatures the rate of HCN displacement increases rapidly. Determinations were made on solutions that gradually warmed up during the HCN collection period from an initial temperature of about 9.5 °C to a final temperature of 14 °C. The precision of these measurements was comparable with that for solutions held at a constant temperature of 22 °C. Therefore, refrigerated samples need not be warmed to a constant temperature but can be transferred to a test apparatus for immediate HCN analysis. Under all circumstances, however, it is essential that standard cyanide solutions be run under the same test conditions along with the unknown solutions to define an appropriate calibration curve relating the quantity of HCN collected to the known HCN concentration.

When the time from addition of a test solution to a Fernbach flask to initiation of a 2-h collection period was varied from near 0 to 2 h, the quantity of HCN collected was virtually the same. An equilibration time of 15–30 min was normally used, however, just before a 2-h collection period. When making cyanide determinations on solutions of very low HCN concentration a longer collection period may be needed to concentrate enough cyanide to make an accurate colorimetric determination. The amount of HCN collected from a test solution was shown to be directly and linearly related to the duration of the collection period. When the test solution volume was between 250 and 1500 mL, the quantity of HCN collected was essentially constant. The displacement of HCN from a solution is apparently not markedly affected by surface area since for this volume change the surface area for the test solutions decreases from about 300 to 250 cm^2.

The results with the diffusion collection system were at least as satisfactory as those with the vapor-phase-equilibration system. The diffusion procedure appears well suited to the routine measurement of HCN since it requires a minimum of sample manipulation, requires no special apparatus, serves to reduce chances of interfering chemical reactions by isolating and concentrating evolved HCN, and has adequate sensitivity and precision.

pK for HCN. The thermodynamic equilibrium constant (pK) of HCN in aqueous solution was determined as a function of temperature over the range of 5–30 °C. The three test solutions at each temperature used to define this relationship contained free cyanide concentrations of about 100 μg/L as HCN. The solutions were prepared with deionized water and had borate buffered pH values of approximately 9.0, 9.3, and 9.7. The HCN displacement rate was determined for each test solution by the vapor-phase-equilibration method, and the molecular HCN concentration was calculated from the appropriate distribution coefficient. The apparent mean pK values for HCN(aq) determined for various cyanide solutions with mean temperatures of 5.1, 10.0, 14.9, 20.1, 25.0, and 30.0 °C were 9.629, 9.533, 9.421, 9.337, 9.220, and 9.145, respectively. The corresponding standard deviations were 0.0135, 0.0048, 0.0066, 0.0039, 0.0150, and 0.0109.

The rate of HCN displacement was approximately the same for similar solutions prepared with deionized water or various natural waters. Therefore, the proposed relationship between the apparent ionization constant of HCN and temperature should be applicable to most fresh waters of normal ionic strength (i.e., μ less than 0.01). The relationship between pK and 1/temperature in degrees Kelvin is an adequate and theoretically justifiable representation of the temperature dependence of the pK for HCN over the experimental tem-

Table II. Fraction of Free Cyanide ($HCN + CN^-$) as Hydrocyanic Acid (HCN) in Aqueous Solutions of Low Ionic Strength (μ less than 0.01)

temp, °C	pH 6.0	pH 6.2	pH 6.4	pH 6.6	pH 6.8	pH 7.0	pH 7.2	pH 7.4
5	1.000	1.000	0.999	0.999	0.999	0.998	0.996	0.994
6	1.000	1.000	0.999	0.999	0.998	0.998	0.996	0.994
7	1.000	1.000	0.999	0.999	0.998	0.997	0.996	0.994
8	1.000	1.000	0.999	0.999	0.998	0.997	0.996	0.993
9	1.000	1.000	0.999	0.999	0.998	0.997	0.996	0.993
10	1.000	1.000	0.999	0.999	0.998	0.997	0.995	0.993
11	1.000	1.000	0.999	0.999	0.998	0.997	0.995	0.992
12	1.000	0.999	0.999	0.999	0.998	0.997	0.995	0.992
13	1.000	0.999	0.999	0.999	0.998	0.997	0.995	0.992
14	1.000	0.999	0.999	0.999	0.998	0.996	0.994	0.991
15	1.000	0.999	0.999	0.998	0.998	0.996	0.994	0.991
16	1.000	0.999	0.998	0.998	0.997	0.996	0.994	0.990
17	1.000	0.999	0.999	0.998	0.997	0.996	0.994	0.990
18	1.000	0.999	0.999	0.998	0.997	0.996	0.993	0.989
19	1.000	0.999	0.999	0.998	0.997	0.996	0.993	0.989
20	1.000	0.999	0.999	0.998	0.997	0.995	0.993	0.988
21	1.000	0.999	0.999	0.998	0.997	0.995	0.992	0.988
22	0.999	0.999	0.999	0.998	0.997	0.995	0.992	0.987
23	0.999	0.999	0.999	0.998	0.997	0.995	0.992	0.987
24	0.999	0.999	0.999	0.998	0.996	0.994	0.991	0.986
25	0.999	0.999	0.999	0.998	0.996	0.994	0.991	0.986
26	0.999	0.999	0.998	0.998	0.996	0.994	0.990	0.985
27	0.999	0.999	0.998	0.997	0.996	0.994	0.990	0.984
28	0.999	0.999	0.998	0.997	0.996	0.993	0.990	0.984
29	0.999	0.999	0.998	0.997	0.996	0.993	0.989	0.983
30	0.999	0.999	0.998	0.997	0.995	0.993	0.989	0.982

temp, °C	pH 7.6	pH 7.8	pH 8.0	pH 8.2	pH 8.4	pH 8.6	pH 8.8	pH 9.0
5	0.991	0.986	0.977	0.964	0.945	0.915	0.872	0.811
6	0.990	0.985	0.976	0.963	0.942	0.911	0.866	0.804
7	0.990	0.984	0.975	0.961	0.939	0.907	0.861	0.796
8	0.989	0.983	0.974	0.959	0.937	0.903	0.855	0.788
9	0.989	0.982	0.973	0.957	0.934	0.899	0.849	0.780
10	0.988	0.982	0.971	0.955	0.931	0.894	0.842	0.771
11	0.988	0.981	0.970	0.953	0.928	0.890	0.836	0.763
12	0.987	0.980	0.968	0.951	0.924	0.885	0.829	0.754
13	0.987	0.979	0.967	0.949	0.921	0.880	0.823	0.745
14	0.986	0.978	0.965	0.946	0.918	0.875	0.816	0.737
15	0.985	0.977	0.964	0.944	0.914	0.870	0.809	0.727
16	0.985	0.976	0.962	0.941	0.910	0.865	0.802	0.718
17	0.984	0.975	0.961	0.939	0.906	0.860	0.794	0.709
18	0.983	0.974	0.959	0.936	0.903	0.854	0.787	0.699
19	0.982	0.972	0.957	0.934	0.899	0.848	0.779	0.690
20	0.982	0.971	0.955	0.931	0.894	0.842	0.771	0.680
21	0.981	0.970	0.953	0.928	0.890	0.836	0.763	0.671
22	0.980	0.969	0.951	0.925	0.886	0.830	0.755	0.661
23	0.979	0.967	0.949	0.922	0.881	0.824	0.747	0.651
24	0.978	0.966	0.947	0.918	0.877	0.818	0.739	0.641
25	0.977	0.964	0.945	0.915	0.872	0.811	0.730	0.631
26	0.976	0.963	0.942	0.912	0.867	0.804	0.722	0.621
27	0.975	0.961	0.940	0.908	0.862	0.798	0.713	0.611
28	0.974	0.960	0.938	0.905	0.857	0.791	0.704	0.601
29	0.973	0.958	0.935	0.901	0.852	0.784	0.696	0.591
30	0.972	0.956	0.933	0.897	0.846	0.777	0.687	0.580

perature range. This relationship can be represented by the regression equation $pK = 3.658 + 1662/T$ with $R^2 = 0.995$ and was used to define pK at various temperatures in subsequent calculations. The pK value determined in the present study, 9.232 at 25 °C, is in good agreement with that determined by Ang (*16*), 9.22, and by Izatt et al. (*17*), 9.21. However, the relationship calculated from data by Izatt et al. (*17*) for the temperature interval 10–30 °C, and as represented by the equation $pK = 1.620 + 2268/T$ with $R^2 = 0.998$, is slightly different from that determined in this study.

The relationship between [HCN]/[free cyanide] is equal to the factor $[H^+]/(K_1 + [H^+])$ or $1/(10^{pH-pK} + 1)$. When both molecular HCN and free cyanide are expressed as HCN, an HCN concentration divided by the appropriate factor will give the free cyanide concentration. Factors presented in Table II define the fraction of free cyanide as molecular HCN at 1.0 °C intervals from 5 to 30 °C and pH values from 6.0 to 9.0 in 0.2-unit intervals.

HCN Determinations in Waters and Wastewaters. The feasibility of directly determining HCN concentrations in water samples was evaluated by use of the diffusion technique. Several ions, two gases, and a few organic compounds commonly found in natural waters and wastewaters were investigated for possible interference with this method.

A substance that would directly interfere with the measurement of HCN must have a significant vapor pressure above its solution, must be collected by an alkaline solution, and must affect the colorimetric determination of cyanide.

Table III. Quantity of HCN Collected by the Diffusion Procedure from Standard Cyanide Solutions of Different pH

buffered pH value[a]	HCN collected,[b] μg	
	predicted[c]	determined
5.99	1.31	1.31
7.62	1.28	1.12
8.45	1.14	1.11
8.71	1.04	1.08
9.07	0.816	0.846
9.29	0.654	0.714
9.36	0.601	0.646
9.50	0.499	0.587
9.67	0.385	0.412

[a] pH controlled with phosphate or borate buffers. [b] HCN collected by 20.5 mL of 0.02 N NaOH in 2 h from 1.5-L solutions containing 25 μg/L free cyanide and at 22 °C. [c] Predicted values based on pK_a = 9.289 at 22 °C.

The colorimetric reaction between cyanide and pyridine, however, is a relatively specific reaction and not very subject to interferences. The presence of ammonia at 50 mg/L NH_3-N, sulfide at 0.50 and 1.0 mg/L S, and phenol at 50 mg/L resulted in only about an 8%, 3%, 13%, and 0% reduction, respectively, in the color developed by the pyridine–barbituric acid method for solutions containing 40 μg/L HCN. Thiocyanate, however, severely affects the determination of cyanide since it is halogenated directly just as free cyanide. The presence of silver and nickel cyanide complexes also gave a positive interference in the direct determination of free cyanide.

A substance could indirectly interfere with the measurement of HCN by contributing free cyanide to the system or affecting the rate at which HCN diffuses from a test solution. The displacement of HCN by diffusion from 1.5-L test solutions containing 25 μg HCN/L was virtually unaffected by the individual presence of the following chemicals: 130 mg/L Cl^-,

Table IV. Determination of HCN by the Diffusion Procedure for Phosphate-Buffered Cyanide Solutions at 20 °C and Containing Complexing Metals

test solution[a]	pH value	amt of total cyanide present (as HCN), μg L^{-1}	HCN concn, μg L^{-1}	
			expected	determined
$ZnSO_4$ + 4NaCN	7.35	25.3	25.3	24.3
$CdSO_4$ + 4NaCN	7.50	24.7	24.7	20.1
$Pb(NO_3)_2$ + 4NaCN	7.50	26.4	26.4	26.0
$K_4Fe(CN)_6$	7.72	1000	~0.0	1.67
$K_4Fe(CN)_6$ + 25 μg/L HCN	7.74	1025	~25.0	25.9
$K_3Fe(CN)_6$	7.74	1000	~0.0	1.53
$K_3Fe(CN)_6$ + 25 μg/L HCN	7.74	1025	~25.0	25.7
$AgNO_3$ + 2NaCN	7.68	500	5.82[b]	4.63
$AgNO_3$ + 2NaCN	7.43	10000	12.3[b]	14.0
$NiSO_4$ + 4NaCN	7.07	5000	190[b]	149
$NiSO_4$ + 4NaCN	7.06	10000	200[b]	154

[a] Iron cyanide solutions were shielded from light. [b] Concentrations based on results for similar solutions as reported by Broderius (*19*).

Table V. Determination of HCN by the Diffusion Procedure for NaCN Spiked Water and Wastewater Samples at 20 °C

sample	pH value	amt of total cyanide added (as HCN), μg L^{-1}	HCN concn, μg L^{-1}	
			expected[a]	determined
Natural Waters				
well	7.92	27.2	26.2	18.8
spring	7.38	27.2	26.9	27.0
creek	6.53	27.2	27.1	26.2
lake	7.85	27.2	26.3	23.4
pond	8.57	27.2	23.1	20.6
Industrial and Muncipal Treatment Effluent				
Plant A[b]				
100% effluent	7.00	0.0	0.0	~0.0
100% effluent	6.80	27.5	27.4	15.9
50% effluent	6.90	27.5	27.4	19.1
25% effluent	7.00	27.5	27.4	23.3
Plant B[c]				
100% effluent	7.55	0.0	0.0	~0.0
100% effluent	7.55	27.0	26.6	11.0
50% effluent	7.65	27.0	26.4	11.3
25% effluent	7.70	27.0	26.4	16.8
Oil Refinery Effluent[d]				
100% effluent	5.90	0.0	0.0	7.8
100% effluent	5.95	28.5	36.3	41.0
50% effluent	6.05	28.5	32.4	33.9
25% effluent	6.15	28.5	30.4	31.2

[a] Expected concentration is equal to that added as NaCN plus that present in the effluent portion; all values adjusted for pH and temperature. [b] Effluent from the Western Lake Superior Sanitary District Treatment Plant, Duluth, MN. [c] Effluent from Mill Creek Wastewater Treatment Plant, Cincinnati, OH. [d] Effluent from the catalytic cracking of Canadian crude oil before any treatment and not including the cooling water portion of the total effluent.

7.4 mg/L SO_4^{2-}, 3.0 mg/L NO_3^-, 100 mg/L SCN^-, 50 mg/L NH_3-N, 0.1 mg/L Na_2S-S, 50 mg/L phenol, 50 mg/L o-cresol, 5 mg/L Zn^{2+}, 5 mg/L Cd^{2+}, 5 mg/L Pd^{2+}, 1.0 mg/L $Fe(CN)_6^{4-}$ or $Fe(CN)_6^{-3}$ as CN in the dark, 100 mL of $^1/_{15}$ M phosphate or borate buffers, and 33 mg/L granular or 0.15 mL/L liquid detergent.

Sulfide at concentrations of 1.0 mg/L Na_2S-S extensively interfered with the determination of HCN. Since it was observed that such a concentration will only have minimal effect on the direct colorimetric procedure for cyanide determination, the interference process must occur in the test solution itself. Possibly sulfide oxidation products, especially polysulfides, react with cyanide to produce thiocyanate (*18*). Therefore, sulfide should be removed from a sample as soon as possible after collection to prevent its potential interaction with cyanide. Recommended procedures for sulfide removal suggest the addition of either lead or cadmium salts (*15*).

The performance of the diffusion method was evaluated with a variety of water and wastewater samples by determining the recovery of cyanide from samples spiked with NaCN and complex cyanides. A summary of the tests with various waters is presented in Tables III–V.

The quantity of HCN collected in NaOH from deionized water solutions buffered at various pH values and containing 25 μg/L free cyanide was generally lower than, but satisfactorily agreed with, the values predicted from a calculated p*K* value of 9.289 for 22 °C (Table III). The results for solutions containing iron cyanide complexes, which are essentially undissociated in the dark, and for those with zinc, cadmium, and lead, which are virtually completely dissociated at dilute concentrations, are in accordance with expectations (Table IV). The results for silver and nickel cyanide complex solutions, in which only a fraction of the total cyanide exists as HCN, are also in reasonable agreement with expected values as determined from earlier work (*19*), which utilized the vapor-phase equilibration procedure for HCN measurement.

The type of sample was most important in determining the percentage recovery of spiked simple cyanide (Table V). For natural water samples, with the exception of very hard well water (296 mg/L as $CaCO_3$), the determined HCN concentrations were essentially equal to the expected values. In most cases the recoveries from spiked effluents were lower than from pure water samples, which resulted in lower determined HCN concentrations than expected. This response may be due to free cyanide-complexing components and other chemical and biological reactions making a portion of the spiked cyanide not present or unavailable for measurement. Therefore measuring the recovery of cyanide added to certain samples is not necessarily a reliable means of studying the suitability of the method for natural water samples. In no instance, however, was a marked positive interference detected when HCN was expected to be absent or in low concentration (Table V). This was also true for an effluent from a copper, cadmium, and zinc plating plant in which no free cyanide was determined following a spike of about 25 μg/L.

The vapor-phase-equilibration method was not deemed as useful as the diffusion procedure in determining low concentrations of HCN. The diffusion method appears to be suitable for the determination of HCN in the microgram-per-liter range since considerable direct and indirect evidence indicates that the method can be used for many types of samples. Even when it is necessary to analyze for HCN in the field, the diffusion method provides a feasible approach.

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